# THE INTRODUCTION OF IODINE INTO SOME AROMATIC AMINES

By

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# INTRODUCTION

The purpose of this work was to try out the substitution of iodine in the ring of some of the anilines, in which at least one other position in the ring had already been filled by substitution, by heating together the iodine and aniline in the presence of pure finely divided calcium carbonate and a small amount of water and ether taken in equal quantities, and to try the reactions of the resulting products with various substances.

Wheeler and his students have used this method in the Yale laboratories for substituting iodine in the ring of toluidines.*
T. H. Vaughn has done some work in this laboratory using this method.** He prepared the mono- and di-iodo derivatives of p-brom-aniline, the mono-iodo-derivative of m-brom-aniline and the di-iodo derida-tive of p-chlor-aniline.

* American Chemical Journal, XLII, 138, 497; XLIV, 449, 501.
** Master's Thesis, 1916.

Among the first reactions tried was that of p-anisidine with aniline. Nothing but a tarry, resinous, waxy substance was obtained. About half of the time devoted to this work was spent in trying to determine the nature of this substance, without any satisfactory results being obtained. It was found that in all of these reactions, more or less of a tarry resinous substance was obtained as well as the desired product. This seems to be characteristic of this method as well as some other methods that have been described for introducing iodine into the benzene ring. Wheeler* mentions obtaining a tarry substance, but dismisses it by saying that nothing was obtained from it. Kerschbaum# mentions obtaining a resinous substance containing iodine as one of his products obtained by treating pseudo-cumidine with iodine monochloride. However he says nothing concerning the structure of the substance. R. L. Datta and N. R. Chatterjee** of Calcutta, in their work on the introduction of iodine into the benzene ring with nitric acid as an oxidiz-

*American Chemical Journal, XLIV, 129.
# Berichte, XXVIII, 2804.
** Jour. Amer. Chem. Soc., XXXIX, 437-440.

ing agent, frequently mention obtaining a yellow or dark viscous substance in addition to their product, but they record no attempt to determine the nature of the substance.

After the attempt to determine the nature of this resinous substance was given up, the method under investigation was tried for the introduction of iodine into the ring of each of the three monochlor-anilines. Some very satisfactory results were obtained and the reactions of the various iodochlor-anilines with different substances were tried out. The method was also tried with 2-4-dichloraniline, o-anisidine, as-m-xylidine, and ps-cumidine with a degree of success.

In all cases when a sufficiently large quantity of the product was obtained, two analyses of the compound were made. Either two nitrogen determinations, two halogen determinations, or one nitrogen and one halogen determination were made. The nitrogen determinations were made by the Kjeldahl method, which is described in every organic text book and requires no further description here. The halogen determinations were made by the liquid ammonia method and since it is not such a widely

known method, a description of the procedure followed is given in connection with the first analysis for halogens.

Enough work was done to show that this method for the introduction of iodine into the benzene ring of anilines is not one of general application, but may be successfully applied for certain compounds, while for others it cannot be used. Not enough work was done to determine just which anilines or which class or classes of anilines could be successfully treated by this method and which ones could not, but "Some General Observations" are placed at the close of this paper which may be helpful to anyone else wishing to continue work along this line.

In concluding this preliminary discussion, the writer wishes to express his gratitude and appreciation to Professor F. B. Dains, under whose supervision this work has been done, for his many helpful suggestions and kindly interest.

## REACTION OF IODINE WITH p-ACETPHENYLENEDIAMINE

Ten grams of p-acetphenylenediamine, twenty grams of iodine, forty c.c. of ether, forty c.c. of water, and ten grams of finely divided calcium carbonate were placed in a flask which was then connected with a reflux condenser and heated on a water bath for about three hours. The iodine reacted with the acetphenylenediamine producing a dark brown substance insoluble in water. It was slightly soluble in alcohol, acetone, pyridine, chloroform, and benzene. It was thought that the dark color might be due to free iodine left uncombined. The brown product was washed with a strong solution of sodium thiosulphate and filtered through bone-black but this failed to remove the dark color. Several re-crystallizations from the above-mentioned solvents failed to make any change in the color. An attempt was made to distill it with steam but without success. The brown substance did not have a definite melting point but passed through a waxy stage between 240° and 250° in changing from solid to liquid. The product was treated with acetic anhydride and a brown substance was obtained which had such a high melting point that it could not be determined using a bath of sulphuric

acid. Upon treating the original product with dry hydrogen chloride gas a product was obtained which could not be melted in a sulphuric acid bath. Two nitrogen determinations were made on the original product and they gave 11.23% and 11.18% respectively. The theoretical percentage of nitrogen in mono-iodo-p-acetphenylenediamine is 10.15%. This is the product that was expected but it is very doubtful if it was obtained. It is more likely that the brown substance was a sort of wax or resin similar to one that will be more fully discussed later under the reaction of iodine with p-anisidine.

| Analysis for nitrogen: | I | II |
|---|---|---|
| Weight watch glass and sample | 7.6267 g. | 7.2295 g. |
| Weight watch glass alone | -7.2295 | 6.4360 |
| Weight sample used | -0.3972 g. | 0.7935 g. |
| **Titration:** | | |
| HCl | 35 c.c. | 50 c.c. |
| NaOH - Lower reading | 12.40 | 18.73 |
| Upper reading | 0.75 | 12.40 |
| NaOH solution used | -11.65 c.c. | 6.33c.c. |
| NaOH factor | 1.19 | |
| Vol. HCl used up by $NH_3$ | -21.62 | 42.47 c.c. |
| 1 c.c. HCl equals | 0.0021 g. $N_2$. | |
| Weight of $N_2$ found | 0.0444 g. | 0.0892 g. |
| Percent $N_2$ found | -11.18 % | 11.23 %. |

## REACTION OF IODINE WITH p-ANISIDINE

Para-anisidine was treated with iodine under the same conditions as explained in the preceding preparations. A black product was obtained which was a waxy resinous substance. It was somewhat soluble in acetone, benzene, chloroform, and pyridine. By using a rather large quantity of pyridine the substance was dissolved and precipitated in a black powdery form by the addition of ice-water. It was thought that the black color might be due to uncombined iodine, but treatment with sodium thiosulphate and sodium bisulphite failed to remove any of the color. The solution in pyridine was boiled with bone-black, filtered and precipitated by the addition of cold dilute ammonium hydroxide, but it remained as black as ever. Treatment with Fuller's earth failed to remove any of the color. The product was not soluble in hot concentrated hydrochloric acid, hence it seemed that no reaction took place. The product did not have a definite melting point but passed through a waxy stage at about 100°- 110°. Analyses for nitrogen gave 3.34% and 3.56% $N_2$. When the product was

treated with benzoyl chloride, iodine was liberated showing that decomposition took place. The product obtained from this reaction, when treated with water gave benzoic acid.

Another small quantity of p-anisidine was treated with iodine under the conditions explained previously and a product was obtained which seened to be a little more sticky and waxy than the first one. It was dissolved in pyridine and then separated by pouring the solution into cold water. The product had a black color as before. An attempt to take the melting point showed that a part of the product appeared to sublime at about 170°, while some of it remained unmelted when the sulphuric acid bath was heated almost to the boiling point.

An attempt was made to find the molar weight of this black substance by the boiling-point method using benzene as the solvent, but it was not suluble enough in benzene as was shown by most of the substance being found undissolved in the apparatus at the end of the determination. Similar troubles were encountered upon trying to use acetone or chloroform as the solvent.

It was thought that probably the color was due to two of the rings of the aniline combining or uniting in some way. As it was impossible to determine the molar weight, this idea was neither verified nor contradicted.

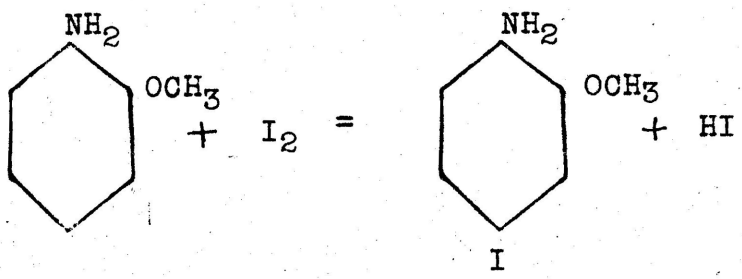
The black product from the second preparation was analyzed for nitrogen. Four determinations gave 7.87%, 7.92%, 7.53%, and 5.68% nitrogen. Mr. H. A. Nelson, working in this laboratory on iodine determinations with liquid ammonia, analyzed it for iodine. Two analyses gave 55.24% and 57.76%.

From the discrepencies in the nitrogen analyses of the products obtained from the different preparations, the writer is of the opinion that the black product does not consist of a single definite chemical compound, but rather an indefinite mixture of different compounds.

## REACTION OF o-ANISIDINE WITH IODINE.

Some o-anisidine was distilled in order to purify it and then ten grams of this freshly distilled material were mixed with twenty grams of iodine, fifteen grams of powdered calcium carbonate, and forty c.c. each of water end ether in a 250 c.c. wide-mouth flask and heated for four or five hours on a water bath under a reflux condenser. The o-anisidine and iodine reacted to form mono-iodo-o-anisidine.

It was not definitely proved in which position the iodine was substituted, but it was assumed that it entered para to the $NH_2$ group. The basis for this assumption is that in ortho and meta chlor-aniline the iodine entered para to the $NH_2$ group. Hence it would seem that in this case also the iodine should enter para to the $NH_2$ group. The reaction based upon this assumption is as follows:




$$CaCO_3 + 2HI = CaI_2 + H_2O + CO_2$$

The product was separated by steam distillation and came over as a reddish brown oil which solidified upon cooling and standing over night. During the night some fine needle-like crystals with a pinkish tinge were formed. Some of these pure crystals were separated, dried on a porous plate and the melting point found to be 49°.

The solid material was filtered from the water, dissolved in alcohol and boiled with animal charcoal to remove the color. The material was precipitated by the addition of ice and ice-water. This precipitate was somewhat pink in color. It was dried and analyzedfor nitrogen as follows:

Weight watch glass and sample - - 5.3055 g.
Weight watch glass alone- - - - - 5.0380
Weight sample used - - - - - - - - 0.2675 g.

Titration:

HCl- - - - - - - - - - - - - - - - - 10 c.c.

NaOH - - Burette readings: Lower - 9.70
Upper - 2.45
NaOH solution used - - - - - - - - - 7.25
NaOH factor - - - - - - - - - - - - 1.05
HCl used up by $NH_3$ - - - - - - - - - 2.39 c.c.
1 c.c. HCl equals - - - - - - - 0.00626 g. $N_2$.
Weight $N_2$ found - - - - - - - - - - -0.01496 g.
Percent $N_2$ found - - - - - - - - - - 5.29 %
Calculated for $C_7H_8ONI$ - - - - - - - 5.62 %.

The p-iodo-anisidine was analyzed for iodine by the liquid ammonia method described below with the following results:

Weight watch glass and sample - - - 5.0880 g.
Weight watch glass alone - - - - - 5.0380
Weight sample used - - - - - - - - 0.0500

Titration:

$AgNO_3$ - - Lower reading - - - - - - 47.70
Upper reading - - - - - - 24.50
$AgNO_3$ solution used - - - - - - - - 23.20 c.c.

$NH_4NCS$ - Lower reading - - - - - - 15.20
Upper reading - - - - - - 0.00
$NH_4NCS$ solution used - - - - - - - 15.20 c.c.

1 c.c. $NH_4NCS$ sol. equals 1 c.c. $AgNO_3$ sol.

$AgNO_3$ sol. used to ppt. iodine - - 15.20 c.c.

1 c.c. N/40 $AgNO_3$ sol. equals 0.003173 g. $I_2$.

Weight of iodine found - - - - - -0.025384 g.

Percent iodine found - - - - - - - 50.76 %

Calculated- - - - - 51.00 %.

LIQUID AMMONIA METHOD FOR HALOGEN DETERMINATIONS.

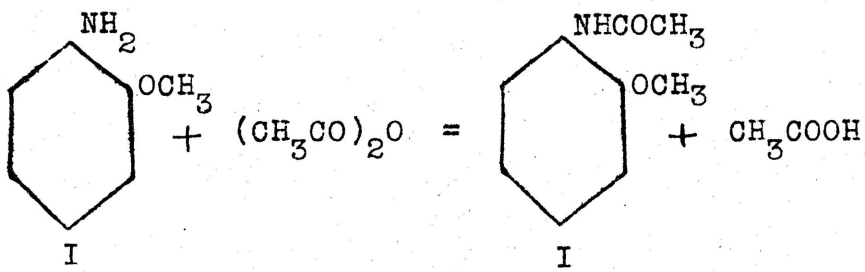
A small quantity of the substance (usually less than 0.1 gram) should be accurately weighed and placed in a Dewar bulb and about 30 c.c. of liquid ammonia added. When the material is in solution a small piece of metallic sodium is added. This reacts with the halogen in the material to

form the sodium halide salt. The solution should be stirred frequently for about an hour or so and then let stand until all of the ammonia has evaporated. The dry product is then washed out into a beaker with water and acidified with nitric acid. A measured volume of a standard solution of $AgNO_3$, somewhat in excess of that calculated to precipitate the halogen, is then added from a burette. The mixture should then be heated to coagulate the precipitate, and filtered. The excess $AgNO_3$ in the filtrate is then titrated with $NH_4NCS$ solution, using 5 c.c. of a solution of ferric alum as indicator. The first reddish tinge indicates the end-point. At times the solution itself has a reddish tinge making this point somewhat hard to determine. The volume of $NH_4NCS$, expressed in terms of the $AgNO_3$ solution, subtracted from the $AgNO_3$ solution gives the volume of $AgNO_3$ solution used to precipitate the halogen. If more than one halogen is present, the volume of $AgNO_3$ solution used must be divided between them according to the number of atoms of each in the formula for the compound before calculating the amount of each present.

REACTION OF p-IODO-o-ANISIDINE WITH ACETIC ANHYDRIDE.

About one and one-half grams of p-iodo-o-anisidine were treated with acetic anhydride. A reaction took place immediately. The product was heated with a slight excess of the anhydride on a water bath under a reflux condenser for about twenty minutes to insure that the reaction was complete.

The reaction is as follows:




The product was dissolved in alcohol and precipitated by the addition of ice and ice-water. The melting point of the crystals was found to be 176°.

Analysis for nitrogen:

Weight watch glass and sample - - 9.0670 g.
Weight watch glass alone - - - - 8.7670
Weight sample used- - - - - - - - 0.3000 g.

Titration:

HCl - - - - - - - - - - - - - - - - - - 10 c.c.

NaOH - - Burette readings: Lower- 24.10
Upper- 16.80
NaOH solution used- - - - - - - - - 7.30 c.c.

NaOH factor - - - - - - - - - - - - - 1.05

HCl used up by $NH_3$ - - - - - - - - 2.34 c.c.

1 c.c. HCl equals - - - - - - - 0.00626 g. $N_2$.

Weight of $N_2$ found - - - - - - - - 0.01465 g.

Percent $N_2$ found - - - - - - - - - - - 4.88 %

Calculated for $C_9H_{10}O_2NI$ - - - - - - - 4.81 %.

Analysis for iodine:

| | |
|---|---|
| Weight watch glass and sample - - | 5.0880 g. |
| Weight watch glass alone- - - - - | 5.0380 |
| Weight sample used- - - - - - - - | 0.0500 g. |

Titration:

| | |
|---|---|
| $AgNO_3$ - - Lower reading - - - - - | 40.90 |
| Upper reading - - - - - | 29.50 |
| Volume $AgNO_3$ sol. used - - - - - | 11.40 c.c. |

| | |
|---|---|
| $NH_4NCS$ - -Lower reading - - - - - | 4.50 |
| Upper reading - - - - - | 0.00 |
| $NH_4NCS$ sol. used - - - - - - - - - | 4.50 c.c. |

1 c.c. $NH_4NCS$ sol. equals 1 c.c. $AgNO_3$ sol.

$AgNO_3$ sol. used to ppt. iodine - - 6.90 c.c.

1 c.c. N/40 $AgNO_3$ sol. equals 0.003173 g. $I_2$.

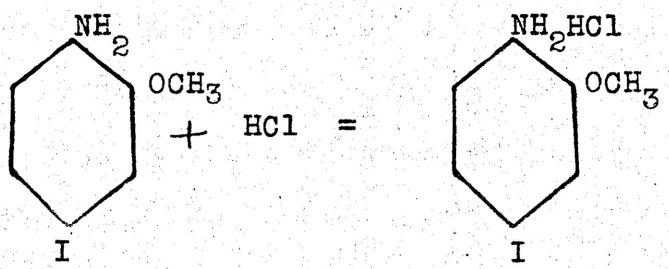
Weight of iodine found - - - - - 0.021894 g.

Percent iodine found - - - - - - 43.79 %

Calculated - - - 43.64 %.

PREPARATION OF p-IODO-o-ANISIDINE HYDROCHLORIDE.

About one and one-half grams of p-iodo-o-anisidine were dissolved in benzene and dry hydrogen chloride gas passed through the solution until precipitation was complete. The following reaction took place:




The precipitate was dried on a porous plate and the melting point found to be 180°. The material had a reddish tinge.

The substance was analyzed for HCl by dissolving it in alcohol and titrating with standard NaOH solution.

| Analysis: | I | II |
|---|---|---|
| Weight watch glass and sample | 5.5380 g. | 5.5380 g. |
| Weight watch glass alone | 5.0380 | 5.0380 |
| Weight sample | 0.5000 g. | 0.5000 g. |
| Burette readings: Lower | 4.75 | 8.20 |
| Upper | 1.25 | 4.75 |
| NaOH solution used | 3.50 c.c. | 3.45 c.c. |

1 c.c. NaOH equals 0.0184 g. HCl.

| | | |
|---|---|---|
| Weight of HCl found | 0.0644 g. | 0.06348 g. |
| Percent HCl found | 12.88 % | 12.70 % |
| Theoretical | 12.78 %. | |

## PREPARATION OF o-CHLORANILINE.

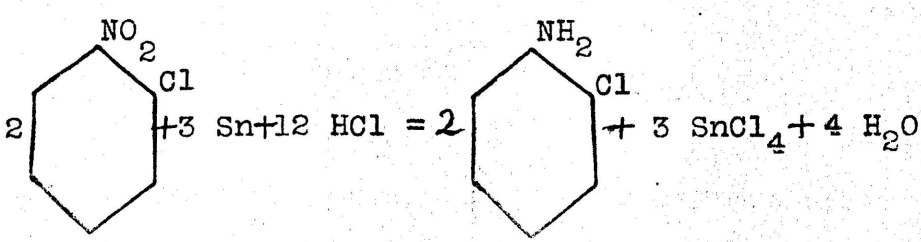
O-chloraniline was prepared from o-chlornitrobenzene by reduction according to the directions given by Gatterman for the preparation of aniline by the reduction of nitrobenzene.

A mixture of 30 grams of tin and 20 grams of o-chlornitrobenzene were placed in a round two-liter flask fitted with an air condenser. To this was gradually added 75 grams of concentrated hydrochloric acid, in 10 c.c. portions with shaking and cooling between additions. However, this reaction is not as violent as the reduction of ordinary nitrobenzene by this method.

In order to insure complete reduction the mixture was finally heated on a water bath for about an hour. To separate the free o-chloraniline about 100 c.c. of water were added to the warm solution, then a solution of 150 grams of caustic soda in 200 c.c. of water were gradually added. The flask was cooled between additions of the caustic soda solution in order to prevent its getting too hot. The mixture was then steam distilled, and the o-chloraniline passed over with steam and collected under the water. About 500 c.c. of the distillate

were collected and shaken with 125 grams of sodium chloride until the salt had all dissolved. The aniline was then extracted with ether. The ethereal solution was dried by shaking it with a few pieces of solid potassium hydroxide, the ether was evaporated and the o-chloraniline subjected to distillation. A fraction, yellow in color, and boiling between 195° and 210° was collected. The greater part of the fraction boiled at about 204° - 206°. The boiling point of o-chloraniline is 207°. Thirteen grams of o-chloraniline were obtained. The theoretical amount would have been sixteen grams.

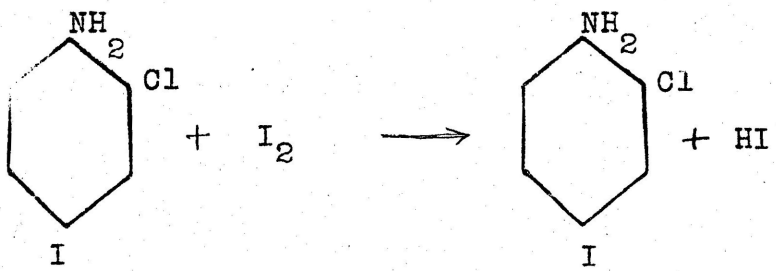
The reaction is as follows:




A second quantity of o-chloraniline was prepared starting with three times the quantities of materials mentioned above and the process carried out as indicated. Forty grams of o-chloraniline were obtained from this preparation.

## REACTION OF o-CHLORANILINE WITH IODINE.

Twelve grams of o-chloraniline, twenty-five grams of iodine, fifteen grams of powdered calcium carbonate, and forty c.c. each of water and ether were mixed in a 250 c.c. wide mouth flask and heated for about three hours on a water bath under a reflux condenser. The o-chloraniline and iodine reacted to form o-chlor-p-iodo-aniline according to the following equation.



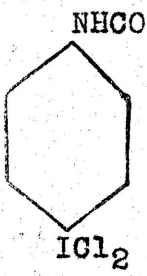

$$CaCO_3 + 2HI = CaI_2 + H_2O + CO_2.$$

The 2-chlor-4-iodo- aniline was separated by steam distillation. It came over as a brown oil which solidified upon cooling. A small amount of black waxy resin was left behind in the distilling flask. The solid product was filtered from the water which came over with it, dissolved in alcohol, and boiled with animal charcoal to remove the color. After filtering, it separated out in white crystals upon the addition of ice-water. The melting point of these crystals was found to be 73°.

| Analyses for nitrogen: | I | II |
|---|---|---|
| Weight watch glass and sample | 9.0670 g. | 9.0670 g. |
| Weight watch glass alone | 8.7670 | 8.7670 |
| Weight sample used | 0.3000 g. | 0.3000 g. |
| **Titration:** | | |
| HCl | 10 c.c. | 10c.c. |
| NaOH - Lower reading | 15.15 | 22.10 |
| Upper reading | 8.15 | 15.15 |
| NaOH solution used | 7.00 c.c. | 6.95 c.c. |
| NaOH factor | 1.05 | |
| Vol. HCl used up by $NH_3$ a a | 2.65 c.c. | 2.70 cc, |
| 1 c.c. HCl equals | 0.00626 g. $N_2$. | |
| Weight of $N_2$ found | 0.01659 g. | 0.01692 g. |
| Percent $N_2$ found | 5.53 % | 5.64 %. |
| Calculated for $C_6H_5NICl$ | 5.52% | |

PROOF OF CONSTITUTION OF 2-CHLOR-4-IODO-ANILINE

Upon investigation it was found that Werner and Caldwell had previously prepared and described a compound which they said was 2- or 3-chlor-4-iodo-aniline. They prepared their compound in the following manner:




was heated at 105° for several hours. one of the Cl went into the

ring, the other being split off by the H displaced forming HCl and 2- or 3-chlor-4-iodo-acetanilide, with a melting point of 144°. Upon hydrolysis this compound broke up forming 2- or 3-chlor-4-iodo-aniline with a melting point of 73°. They obtained the picrate of their compound and its melting point was 132°. 5hey also treated their compound with phenyl mustard oil and obtained the diphenylthiourea which melted at 159°.*

The writer treated separate portions of his compound with acetic anhydride, picric acid, and phenyl mustard oil respectively, and obtained the acetanilide melting at 144°, the picrate melting at 133°, and the diphenylthiourea melting at 158°.

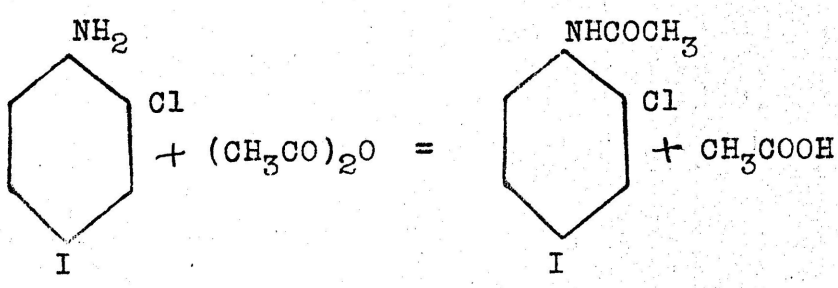
These results prove, without question, that the compound made by Werner and Caldwell and that obtained by the writer are the same. Since they started with the iodine in the para position and the writer started with chlorine in the ortho position, the constitution of the compound prepared by 2erner and Caldwell and that obtained by the writer is proved to be 2-chlor-4-iodo-aniline.

* Chemisches Zentralblatt 1907 (1) 1198. Jour. Chem. Soc. XCI, 246. (This reference was not available for the writer's use).

## REACTION OF 2-CHLOR-4-IODO-ANILINE WITH ACETIC ANHYDRIDE.

The acetyl derivative of 2-chlor-4-iodo-aniline was prepared by heating about three grams of the aniline with an equivalent quantity of acetic anhydride in a small flask on a water bath under a reflux condenser for about half an hour. The product was crystallized from alcohol and the melting point determined. The substance melted at 144°.

The reaction is as follows:




Analysis for nitrogen:

| | |
|---|---|
| Weight watch glass and sample | 9.0630 g. |
| Weight watch glass alone | -8.7670 |
| Weight sample used | 0.2960 g. |

Titration:

| | |
|---|---|
| HCl | 10 c.c. |
| NaOH - Lower reading | 22.15 |
| Upper reading | 14.85 |
| NaOH solution used | 7.30 c.c. |
| NaOH factor | 1.05 |
| HCl used up by $NH_3$ | 2.34 c.c. |
| 1 c.c. HCl equals | 0.00626 g. $N_2$. |

Weight of $N_2$ found - - - - - - 0.01465 g.

Percent $N_2$ found - - - - - - - - - - 4.95 %

Calculated for $C_8H_7ONICl$ - - - - - 4.74 %.

Analysis for iodine and chlorine:

Weight watch glass and sample - - 5.0880 g.
Weight watch glass alone - - - - 5.0380
Weight sample used - - - - - - - - 0.0500 g.

Titration:

$AgNO_3$ - - Lower reading - - - - 18.55
Upper reading - - - - 0.00
Vol. $AgNO_3$ sol. used - - - - - - 18.55 c.c.

$NH_4NCS$ - - Lower reading - - - - 5.15
Upper reading - - - - 0.00
Vol. $NH_4NCS$ sol. used - - - - - 5.15 c.c.

1 c.c. $NH_4NCS$ sol. equals 1 c.c. $AgNO_3$ sol.

$AgNO_3$ sol. used to ppt. halogens 13.40 c.c.

" " " " " iodine - 6.70

" " " " " chlorine 6.70

1 c.c. N/40 $AgNO_3$ sol. equals 0.003173 g. $I_2$.

" " " " " " 0.0008865 g. $Cl_2$.

Weight of iodine found - - - - 0.02126

" " chlorine " - - - - 0.00594

Percent iodine found - - - - 42.52 %

calculated - - 42.98 %

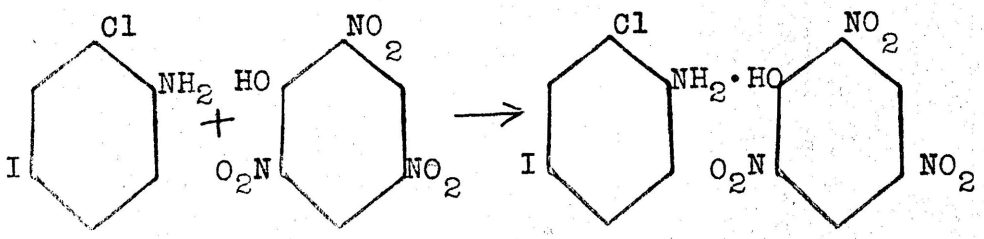
Percent chlorine found - - - 11.88 %

calculated - 12.01 %.

## REACTION OF 2-CHLOR-4-IODO-ANILINE WITH PICRIC ACID.

The picrate of 2-chlor-4-iodo-aniline was prepared by dissolving 2.3 grams of picric acid and 2.6 grams of the aniline separately in alcohol and then mixing them in a small flask which was then heated for about thirty minutes on a water bath under a reflux condenser. Upon cooling, the 2-chlor-4-iodo-aniline-picrate separated out in fine yellow crystals. The product was recrystallized from hot alcohol and the melting point determined. The substance melted at 133°.

The reaction is as follows:




Analysis for nitrogen:

| | |
|---|---|
| Weight watch glass and sample - - | 5.3350 g. |
| Weight watch glass alone - - - - | 5.0350 |
| Weight sample used - - - - - - - | 0.3000 g. |

Titration:

| | |
|---|---|
| HCl - - - - - - - - - - - - - - - - - | 10 c.c. |
| NaOH - - Lower reading - - - - - | 8.40 |
| Upper reading - - - - - | 4.15 |
| NaOH solution used - - - - - - - | 4.25 c.c. |

NaOH factor - - - - - - - - - - - 1.05

HCl used up by $NH_3$ - - - - - - - -5.54 c.c.

1 c.c. HCl equals - - - - - 0.00626 g. $N_2$.

Weight of $N_2$ found - - - - - 0.03468 g.

Percent $N_2$ found - - - - - - - 11.56 %

Calculated for $C_{12}H_8O_7N_4Cl$ - 11.60 %.

Analysis for iodine and chlorine:

Weight watch glass and sample - - 5.0880
Weight watch glass alone - - - - 5.0380
Weight sample - - - - - - - - - - 0.0500

Titration:

$AgNO_3$ - - Lower reading - - - - - 15.85
Upper reading - - - - - 3.35
Volume $AgNO_3$ sol. used - - - - - -12.50

$NH_4NCS$ - Lower reading - - - - - 6.30
Upper reading - - - - - 2.20
Volume $NH_4NCS$ sol. used - - - - - 4.10

1 c.c. $NH_4NCS$ sol. equals 1 c.c. $AgNO_3$ sol.

$AgNO_3$ sol. used to ppt. halogens - 8.40
" " " " " iodine - 4.20
" " " " " chlorine - 4.20

1 c.c. N/40 $AgNO_3$ sol. equals 0.003173 g. $I_2$.
" " " " " " 0.0008865 g. $Cl_2$.

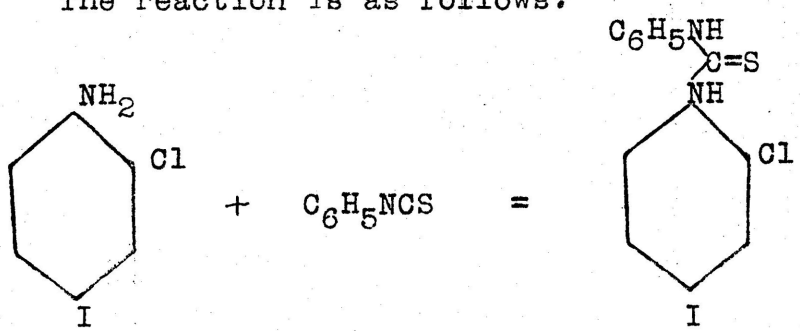
Weight of iodine found - - - - - - - - 0.013326
" " chlorine found - - - - - - - 0.037133

Percent iodine found - - - - - - - - -- -26.65 %
calculated - - - - - - - 26.30 %
Percent chlorine foumd - - - - - - - - 7.43 %
calculated - - - - - -- 7.34 %.

## REACTION OF 2-CHLOR-4-IODO-ANILINE WITH PHENYL MUSTARD OIL.

Three grams of the 2-chlor-4-iodo-aniline were dissolved in alcohol and treated with five c.c. of phenyl mustard oil. The mixture was contained in a small flask and was heated on a water bath under a reflux condenser for about twenty minutes. Upon cooling a solid product crystallized out. This was filtered out and dried on a porous plate to remove the excess oil. This product was very hard to purify. It was crystallized from the gasoline twice, and from alcohol three times before a constant melting point was obtained. The melting point obtained was 158°.

The reaction is as follows:




Analysis for nitrogen:

| | |
|---|---|
| Weight watch glass and sample - - | 8.9550 g. |
| Weight watch glass alone - - - - | -8.7670 |
| Weight sample used - - - - - - - | 0.1880 g. |

Titration:

HCl - - - - - - - - - - - - - - - - - 10 c.c.

NaOH - -Lower reading - - - - 14.85
Upper reading - - - - 7.41
NaOH solution used - - - - - - 7.44 c.c.

NaOH factor - - - - - - - - - - 1.05

HCl used up by $NH_3$ - - - - - - - 2.19 c.c.

1 c.c. HCl equals - - - - - 0.00626 g. $N_2$.

Weight of $N_2$ found - - - - - 0.01371 g.

Percent $N_2$ found - - - - - - - 7.29 %

Calculated for $C_{13}H_{10}N_2ICIS$ - 7.20 %.

Analysis for iodine and chlorine:

Weight watch glass and sample - - - 5.0880 g.
Weight watch glass alone - - - - - 5.0380
Weight sample used - - - - - - - - 0.0500 g.

Titration:

$AgNO_3$ - - - Lower reading - - - - - 18.25
Upper reading - - - - - 0.50
$AgNO_3$ solution used - - - - - - - - 17.75 c.c.

$NH_4NCS$ - - Lower reading - - - - - 7.55
Upper reading - - - - - 0.00
$NH_4NCS$ solution used - - - - - - - - 7.55 c.c.

1 c.c. $NH_4NCS$ sol. equals 1 c.c. $AgNO_3$ sol.

$AgNO_3$ sol. used to ppt. halogens - 10.20 c.c.

" " " " " iodine - - - 5.10 c.c.

" " " " " chlorine - - 5.10 c.c.

1 c.c. N/40 $AgNO_3$ sol. equals 0.003173 g. $I_2$.

" " " " " " 0.0008865 g. $Cl_2$.

Weight of iodine found - - - - - 0.01618 g.

Weight of chlorine found - - - 0.00452 g.

Percent iodine found - - - - - - 32.36 %

Calculated - - - 32.69 %

Percent chlorine found - - - - - 9.04 %

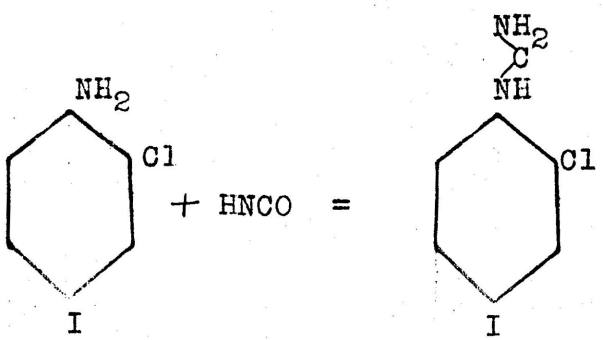
Calculated - - - - 9.14 %.

## REACTION OF 2-CHLOR-4-IODO-ANILINE WITH POTASSIUM CYANATE.

Two grams of the 2-chlor-4-iodo-aniline were dissolved in glacial acetic acid. Two grams of potassium cyanate were dissolved in a separate portion of glacial acetic acid and the two solutions were then mixed. The mixture was allowed to stand with occasional warming, and the two substances reacted to form 2-chlor-4-iodo-phenylurea. This substance was crystallized from alcohol three times and the melting point found to be 175°.

The reaction is as follows:

$$KNCO + CH_3COOH = HNCO + CH_3COOK$$



Analysis for iodine and chlorine:

| | | |
|---|---|---|
| Weight watch glass and sample - - | 5.0880 | 5.0880 |
| Weight watch glass alone - - - - | 5.0380 | 5.0380 |
| Weight sample - - - - - - - - - - | 0.0500 | 0.0500 |

Titration:

| | | |
|---|---|---|
| $AgNO_3$ - - Lower reading - - - - - | 25.35 | 40.60 |
| Upper reading - - - - - | 10.05 | 25.35 |
| Volume $AgNO_3$ sol. used - - - - - | 15.30 | 15.25 |
| $NH_4NCS$ - Lower reading - - - - - | 3.15 | 4.80 |
| Upper reading - - - - - | 1.25 | 3.15 |
| Vol. $NH_4NCS$ sol. used - - - - - | 1.90 | 1.65 |

1 c.c. $NH_4NCS$ sol. equals 1 c.c. $AgNO_3$ sol.

| | | |
|---|---|---|
| $AgNO_3$ sol. used to ppt. halogens- | 13.40 | 13.60 |
| " " " " " iodine - - | 6.70 | 6.80 |
| " " " " " chlorine- | 6.70 | 6.80 |

1 c.c. N/40 $AgNO_3$ sol. equals 0.003173 g. iodine.

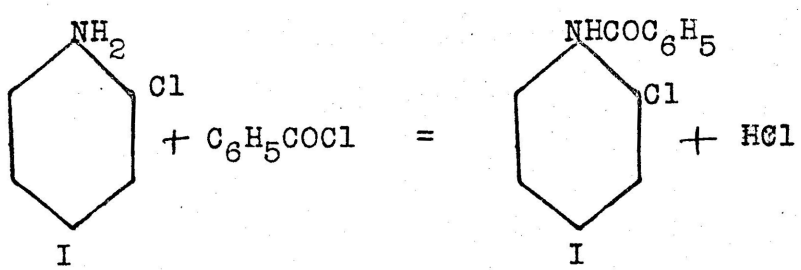
" " " " " " 0.0008865 g. chlorine.

| | | |
|---|---|---|
| Weight of iodine found - - - - | 0.02126 g. | 0.021576 g. |
| " " chlorine " - - - - | 0.00594 | 0.006028 |
| Percent iodine found - - - - - | 42.52 | 43.15 |
| calculated - - - | 42.83 | |
| Percent chlorine found - - - - | 11.88 | 12.05 |
| calculated - - - | 11.97 | |

## REACTION OF 2-CHLOR-4-IODO-ANILINE WITH BENZOYL CHLORIDE.

Three grams of the 2-chlor-4-iodo-aniline were dissolved in a few c.c. of benzene and about 5 c.c. of benzoyl chloride added. The mixture was heated on a water bath under a reflux condenser for about twenty minutes. At the end of this time a solid product had formed in the flask. The solid was filtered out and dissolved in hot gasoline, from which it crystallized upon cooling. It was recrystallized from hot gasoline forming fine white needle like crystals. The product was also found to be very slightly soluble in cold alcohol while it was readily soluble in hot alcohol. It was then recrystallized from hot alcohol. The melting point was taken after each recrystallization and found to be 165° after each of the last two.

The reaction is as follows:

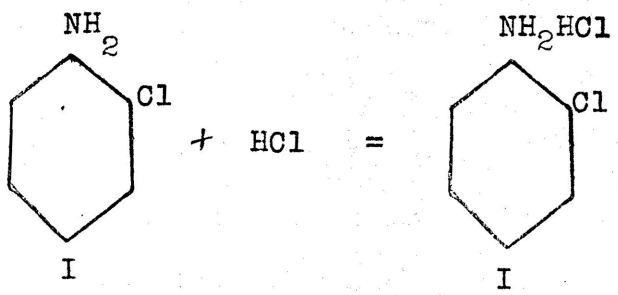


| Analysis for nitrogen: | I | II |
|---|---|---|
| Weight watch glass and sample | 9.0629 | 5.3380 |
| Weight watch glass alone | 8.7669 | 5.0380 |
| Weight sample used | 0.2960 | 0.3000 |
| **Titration:** | | |
| HCl | 20 c.c. | 10 c.c. |
| NaOH - Burette readings: Lower | 24.30 | 21.10 |
| Upper | 8.27 | 13.45 |
| NaOH solution used | 16.03 | 7.65 |
| NaOH factor | 1.13 | 1.05 |
| HCl used up by $NH_3$ | 1.89 c.c. | 1.97 c.c. |
| 1 c.c. HCl equals 0.00626 g. $N_2$. | | |
| Weight of $N_2$ found | 0.01183 g. | 0.01233 g. |
| Percent $N_2$ found | 3.99 % | 4.11 % |
| Calculated for $C_{13}H_9ONICl$ | 3.92 %. | |

## REACTION OF 2-CHLOR-4-IODO-ANILINE WITH HYDROGEN CHLORIDE.

Two grams of the 2-chlor-4-iodo-aniline were dissolved in benzene and dry hydrogen chloride gas passed into the solution until precipitation was complete. The white product was removed by filtration and dried upon a porous plate. An attempt to determine its melting point showed that it decomposed with the liberation of iodine at about 190°.

The reaction for the formation of the hydrochloride is as follows:




The salt was analyzed for HCl by titrating it with standard NaOH solution. It was found that the substance was not soluble enough in water for successful titration so it was dissolved in alcohol and the alcoholic solution diluted with water and titrated.

| Analysis for HCl: | I | II |
|---|---|---|
| Weight watch glass and sample | 9.2670 g. | 9.2557 g. |
| Weight watch glass alone | 8.7670 | 8.7670 |
| Weight of sample | 0.5000 g. | 0.4887 g. |
| Burette readings: - Lower | 39.12 c.c. | 42.44 c.c. |
| Upper | 35.74 | 39.12 |
| NaOH solution used | 3.38 c.c. | 3.32 c.c. |

1 c.c. NaOH solution equals 0.0184 g. HCl.

| | | |
|---|---|---|
| Weight of HCl found | 0.0622 g. | 0.0611 g. |
| Percent HCl found | 12.44 % | 12.50 % |

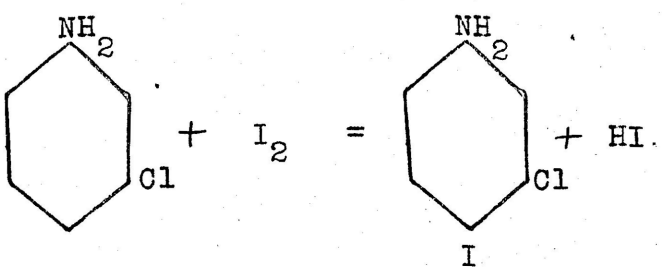
Theoretical - - - - - - - - - - - - - - 12.58 %.

## REACTION OF IODINE WITH M-CHLORANILINE.

Ten grams of m-chlor-aniline, twenty grams of iodine, ten grams of powdered calcium carbonate, and fifty cubic centimeters each of ether and water were mixed in a 250 c.c. wide-mouth flask and heated on a water bath under a reflux condenser for about two hours. After attempting to extract the product with various solvents such as ether, alcohol, benzene, and acetone, it was found that steam distillation was the only satisfactory method that could be employed to separate the product from the tarry resinous material formed at the same time. The most successful way was found to be as follows:- The material was transferred directly from the flask in which it was prepared to a one-liter flask fitted for steam distillation. Steam was passed rapidly through it and the distillate passed through two condensers in series in order to condense it. If any unchanged aniline was present it came over first with the water. For this reason it was found advisable to keep the first half-liter or so of the distillate separate from the remainder as the unchanged aniline present in the product prevents it from crystallizing. It was found to be advisable to keep

any uncombined iodine from entering the distillate. In order to prevent this, a few crystals of sodium thiosulphate were added to the distilling flask before steam was passed in. The distillate which came over was a white milky color. Distillation was continued until the distillate was almost clear. Upon cooling and standing for several hours, the product crystallized out leaving the water clear. After filtration, the product was dissolved in alcohol, boiled with animal charcoal to remove the coloring matter, filtered, and poured into a large quantity of ice-cold water in order to precipitate it. After standing over night it was filtered, the product dried and the melting point found to be 65°. Only a small yield was obtained.

The reaction is as follows:




$$CaCO_3 + 2HI = CaI_2 + H_2O + CO_2.$$

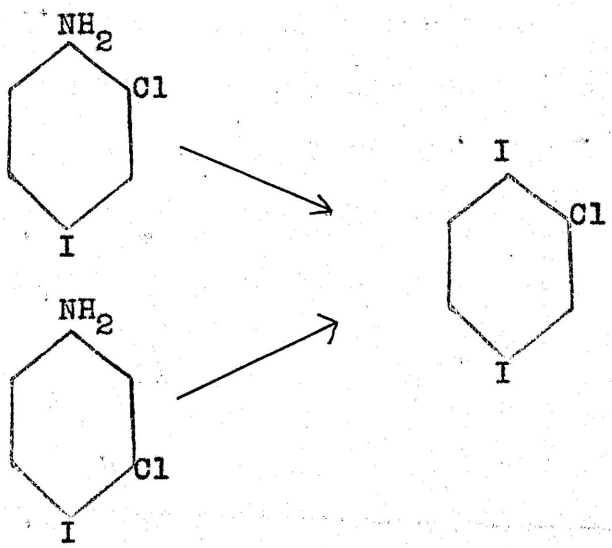
| Analyses for nitrogen: | I | II |
|---|---|---|
| Weight watch glass and sample | 9.0670 g. | 9.0670 g. |
| Weight watch glass alone | 8.7670 g. | 8.7670 g. |
| Weight sample used | 0.3000 g. | 0.3000 g. |
| Titration: | | |
| HCl | 10 c.c. | 10 c.c. |
| NaOH- Lower reading | 9.55 | 16.57 |
| Upper reading | 2.57 | 9.55 |
| NaOH solution used | 6.98 c.c. | 7.02 c.c. |
| NaOH factor | 1.05 | |
| Vol. HCl used up by $NH_3$ | 2.67 c.c. | 2.63 c.c. |
| 1 c.c. HCl equals | 0.00626 g. $N_2$. | |
| Weight of $N_2$ found | 0.01672 g. | 0.01646 g. |
| Percent $N_2$ found | 5.57 % | 5.49 % |
| Calculated for $C_6H_5NICl$ | 5.52 %. | |

PROOF OF CONSTITUTION OF 3-CHLOR-4-IODO-ANILINE.

It was thought that when the iodine entered the ring of m-chloraniline, it went into the position para to the $NH_2$ group. Since it has already been proved that in the iodination of o-chloraniline the iodine went into the ring para to the $NH_2$ group, if the iodine entered para to the $NH_2$ group in the iodination of m-chloraniline, then by replacing the $NH_2$ group of these two chlor-iodo-anilines with iodine the same substance would be obtained, namely

p-di-iodo-o-chlor-benzene.

Each of the above-mentioned chlor-iodo-anilines was diazotized and treated with potassium iodide, thereby replacing the $NH_2$ group of each with iodine. The product from each was found to melt at 51°. Equal quantities of the two products were mixed together and the mixture melted at 51°, showing that the two substances were identical.




PREPARATION OF p-DI-IODO-o-CHLOR-BENZENE.

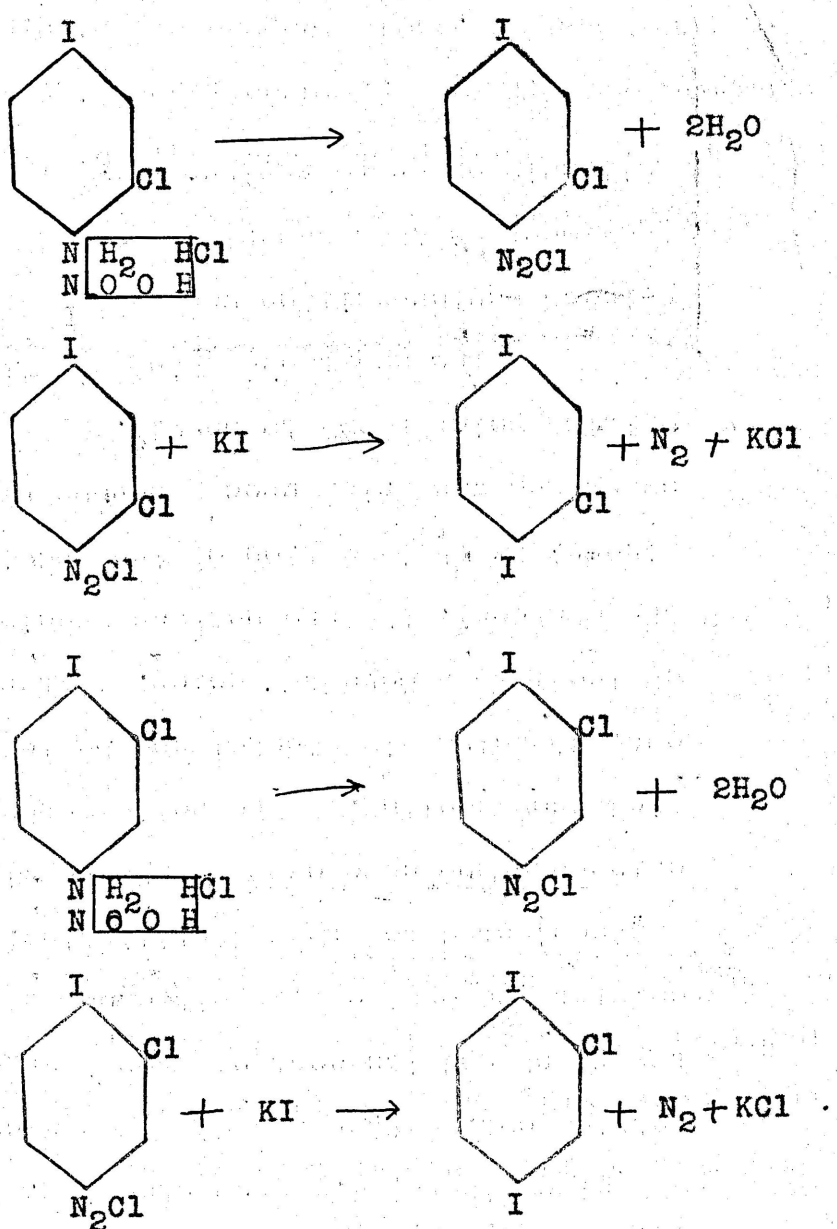
Three grams of p-iodo-o-chlor-aniline were powdered and put into a flask with 7 c.c. hydrochloric acid and 100 c.c. of water. The CHlor-iodo-aniline did not dissolve completely, but what remained undissolved was in a very finely divided form.

The mixture was cooled with ice and a solution of 2.5 grams of sodium nitrite in 25 c.c. of water was added a little at a time until a drop of the solution would turn a starch, potassium iodide paper blue. Then a solution of three grams of potassium iodide was added. There was considerable effervescence due to the escaping nitrogen. Some iodine was also liberated. Upon standing, a very dark oil settled out. After standing for a couple of hours, the flask and its contents were warmed to insure the complete removal of the nitrogen. Then the material was subjected to steam distillation. The p-di-iodo-chlor-benzene came over as a dark oil, which solidified upon cooling. The solid material was filtered out, dissolved in alcohol and boiled with animal chalcoal to remove the color. After filtering out the charcoal, the product was precipitated from the alcohol by the addition of ice and ice-water. The substance was dried upon a porous plate and the melting point found to be $51^{o}$.

The substance which was thought to be p-iodo-m-chlor-aniline was subjected to the same treatment as that described above for p-iodo-o-chlor-anilinein order to replace the $NH_2$ group with I and

the product was found to melt at 51°. When mixed with that obtained above, the mixture melted at 51°, showing that the two substances were identical.

The reactions are as follows:



Analysis for iodine and chlorine:

| | | |
|---|---|---|
| Weight watch glass and sample - - | 13.0245 | 13.0245 |
| Weight watch glass alone - - - - | 12.9745 | 12.9745 |
| Weight sample - - - - - - - - - - | 0.0500 | 0.0500 |

Titration:

| | | |
|---|---|---|
| $AgNO_3$ - - Lower reading - - - - - | 20.35 | 40.70 |
| Upper reading - - - - - | 1.00 | 20.35 |
| Volume $AgNO_3$ sol. used - - - - - | 19.35 | 20.35 |
| $NH_4NCS$ - Lower reading - - - - - | 4.95 | 8.70 |
| Upper reading - - - - - | 2.00 | 4.95 |
| Vol. $NH_4NCS$ sol. used - - - - - | 2.95 | 3.75 |

1 c.c. $NH_4NCS$ sol. equals 1 c.c. $AgNO_3$ sol.

| | | |
|---|---|---|
| $AgNO_3$ sol. used to ppt. halogens | 16.40c.c. | 16.60c.c. |
| " " " " " iodine - | 10.94 | 11.06 |
| " " " " " chlorine- | 5.46 | 5.54 |

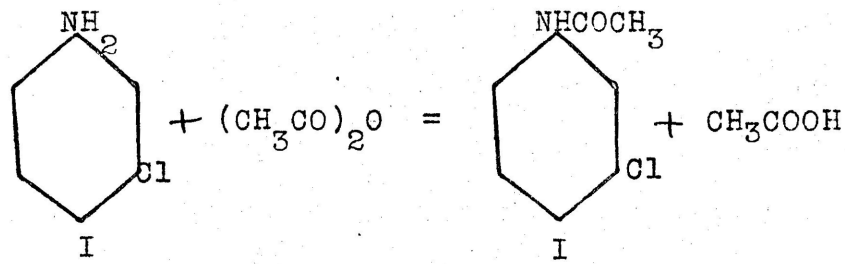
1 c.c. N/40 $AgNO_3$ sol. equals 0.003173 g. iodine.

" " " " " " 0.0008865 g. chlorine.

| | | |
|---|---|---|
| Weight of iodine found - - - - | 0.034713 | 0.03509 |
| " " chlorine " - - - - | 0.00484 | 0.004911 |
| Percent iodine found - - - - - | 69.55 % | 70.18 % |
| calculated - - - | 69.68 % | |
| Percent chlorine found - - - - | 9.68 % | 9.82 % |
| calculated - - - | 9.74 %. | |

## REACTION OF 3-CHLOR-4-IODO-ANILINE WITH ACETIC ANHYDRIDE.

About three grams of 3-chlor-4-iodo-aniline were heated with acetic anhydride for about fifteen minutes. A white crystalline substance was produced. The following reaction took place:



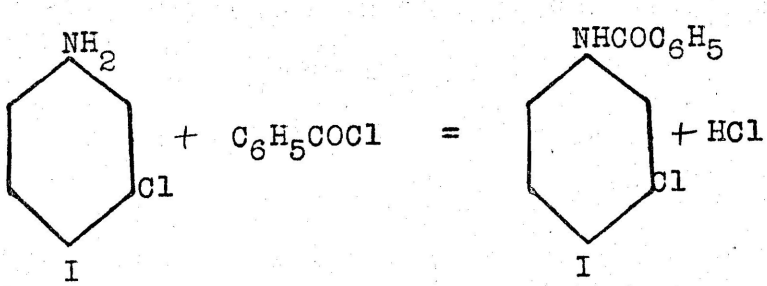

This product was crystallized from alcohol five times in order to purify it. Its melting point was finally found to be constant at 170°.

| Analysis for nitrogen: | I | II |
|---|---|---|
| Wt. weighing bottle with sample | 7.0340 | 6.7462 |
| " " " without " | 6.7462 | 6.4365 |
| Wt. sample used | 0.2878 | 0.3097 |
| **Titration:** | | |
| HCl | 25 c.c. | 25 c.c. |
| NaOH - Lower reading | 16.52 | 31.72 |
| Upper reading | 0.92 | 16.52 |
| NaOH sol. used | 15.60 c.c. | 15.20 cc. |
| NaOH factor | 1.19 | |
| Vol. HCl used up by $NH_3$ | 6.44 c.c. | 7.11 c.c. |
| 1 c.c. HCl equals | 0.0021 g. $N_2$. | |
| Weight of $N_2$ found | 0.0135 g. | 0.0149 g. |
| Percent $N_2$ found | 4.73 % | 4.82 % |
| Theoretical for $C_8H_7NICl$ | 4.72 %. | |

## REACTION OF 3-CHLOR-4-IODO-ANILINE WITH BENZOYL CHLORIDE.

About three grams of 3-chlor-4-iodo-aniline were dissolved in benzene and about five c.c. of benzoyl chloride were added to the solution. A white product formed almost immediately. In order to insure the completion of the reaction the flask and its contents were warmed on a water bath under a reflux condenser for about fifteen minutes. The product was separated by filtration, dried and dissolved in alcohol, from which it was precipitated by the addition of ice cold water. The melting point of the benzanilide was found to be 144°.

The reaction is as follows:




| Analysis for nitrogen: | I | II |
|---|---|---|
| Weight watch glass and sample - | 5.3580 g. | 5.3580 g. |
| Weight watch glass alone - - - | 5.0580 | 5.0580 |
| Weight sample used - - - - - - - | 0.3000 g. | 0.3000 g. |

Titration:

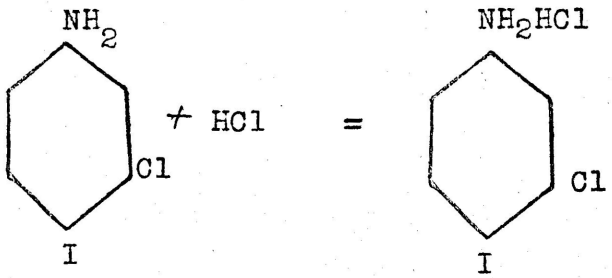
| | | |
|---|---|---|
| HCl - - - - - - - - - - - - - - - - - | 10 c.c. | 10 c.c. |

| | | |
|---|---|---|
| NaOH - Burette readings: Lower | 21.80 | 14.90 |
| Upper | 14.05 | 7.10 |
| NaOH solution used | 7.75 | 7.80 c.c. |
| NaOH factor | 1.05 | |
| HCl used up by $NH_3$ | 1.86 | 1.81 c.c. |
| 1 c.c. HCl equals | 0.00626 g. $N_2$. | |
| Weight of $N_2$ found | 0.01164 g. | 0.01133 g. |
| Percent $N_2$ found | 3.88 % | 3.78 % |
| Calculated for $C_{13}H_9ONICl$ | 3.92 %. | |

## REACTION OF 3-CHLOR-4-IODO-ANILINE WITH HYDROGEN CHLORIDE.

About two grams of 3-chlor-4-iodo-aniline were dissolved in benzene and dry hydrogen chloride gas passed into the solution. A white precipitate was formed. The product was separated from the benzene by filtration and dried on a porous plate. Upon attempting to determine the melting point of the substance, it was found to decompose with the liberation of iodine at about 180°. After this decomposition the substance was liquid at the temperature attained.

The reaction with HCl is as follows:




The salt was analyzed for HCl by titrating it with standard NaOH solution. It was found that the salt was not soluble enough in water for successful titration, so it was dissolved in alcohol and the alcoholic solution diluted with water and then titrated.

| Analysis for HCl: | I | II |
|---|---|---|
| Weight watch glass and sample - | 9.2835 g. | 9.2670 g. |
| Weight watch glass alone - - - | 8.7670 | 8.7670 |
| Weight sample - - - - - - - - - - | 0.5165 g. | 0.5000 g. |
| Burette readings: Lower - - - | 48.96 c.c. | 45.46 c.c. |
| Upper - - - | 45.46 | 42.04 |
| NaOH solution used - - - - - - - | 3.50 c.c. | 3.42 c.c, |

1 c.c. NaOH sol. equals 0.0184 g. HCl.

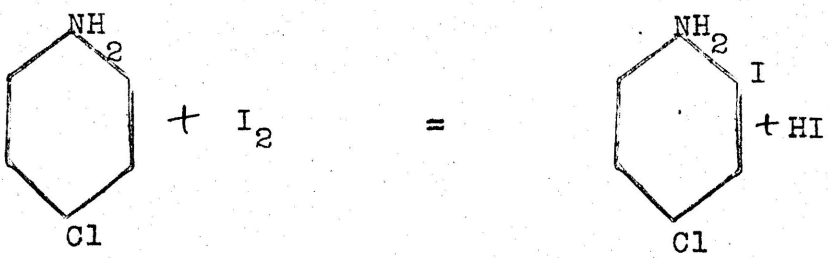
| | | |
|---|---|---|
| Weight of HCl found - - - - - - - | 0.06442 g. | 0.06293 g, |
| Percent HCl found - - - - - - - - | 12.47 % | 12.59 % |
| Theoretical - - - - - - - - - - - - - - - - | 12.58 %. | |

## REACTION OF P-CHLORANILINE WITH IODINE.

Ten grams of p-chloraniline, twenty grams of iodine, ten grams of powdered calcium carbonate, and 40 c.c. each of ether and water were mixed in a 250 c.c. wide-mouth flask and heated on a water bath under a reflux condenser for about two hours. The mixture was then subjected to steam distillation. A dark brown oil came over with the water and a considerable quantity of black tarry material remained behind. The brown oil which came over was separated from the water and let stand in a beaker immersed in ice-water, whereupon it solidified. Upon warming up to room temperature, it again became an oil. The oil was dissolved in gasoline and boiled with animal charcoal, and filtered. This removed much of the dark color. Upon standing for several days, the gasoline evaporated and a small quantity of long needle-like crystals was formed. These were dried upon a porous plate and were found to melt at 45°. A second preparation was made according to the directions given above. The dark oil which came over upon distilling with steam solidified at room temperature after it had been filtered from the water. It was dissolved in alcohol and boiled with animal

charcoal and then filtered. The filtrate was a pale yellow color. A few pieces of ice were put into the flask containing the filtrate and as the ice melted the 4-chlor-2-iodo-aniline separated out in white crystals. Cold water was added to complete the precipitation.

The reaction is as follows:




$$2HI + CaCO_3 = CaI_2 + H_2O + CO_2.$$

Analysis for nitrogen:

| | |
|---|---|
| Weight watch glass and sample | 9.0670 g. |
| Weight watch glass alone | 8.7670 |
| Weight sample | 0.3000 g. |

Titration:

| | |
|---|---|
| HCl | 10 c.c. |
| NaOH - Lower reading | 7.95 c.c. |
| Upper reading | 1.00 |
| NaOH solution used | 6.95 c.c. |
| NaOH factor | 1.05 |
| HCl used up by $NH_3$ | 2.70 c.c. |
| 1 c.c. HCl equals | 0.00626 g. $N_2$. |
| Weight $N_2$ found | 0.01690 g. |
| Percent $N_2$ found | 5.63 % |
| Calculated for $C_6H_5NICl$ | 5.52 %. |

Analysis for iodine and chlorine:

Weight watch glass and sample - - - 8.0835
Weight watch glass alone - - - - - - 8.0335
Weight sample - - - - - - - - - - - - 0.0500

Titration:

$AgNO_3$ - - Lower reading - - - - - - - 19.10
Upper reading - - - - - - - 00.00
Volume $AgNO_3$ sol. used - - - - - - - 19.10

$NH_4NCS$ - Lower reading - - - - - - - 3.30
Upper reading - - - - - - - 0.00
Vol. $NH_4NCS$ sol. used - - - - - - - 3.30

1 c.c. $NH_4NCS$ sol. equals 1 c.c. $AgNO_3$ sol.

$AgNO_3$ sol. used to ppt. halogens - 15.80 c.c.

" " " " " iodine - - - 7.90 c.c.

" " " " " chlorine - - 7.90 c.c.

1 c.c. N/40 $AgNO_3$ sol. equals 0.003173 g. $I_2$.

" " " " " " 0.0008865 g. $Cl_2$.

Weight of iodine found - - - - - - - 0.0250667 g.

" " chlorine " - - - - - - - 0.00700335 g.

Percent iodine found - - - - - - - - 50.13 %

calculated - - - - - 50.07 %

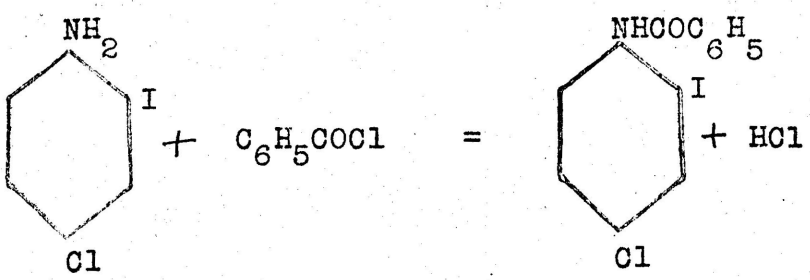
Percent chlorine found - - - - - - -14.01 %

calculated - - - - - 14.00 %.

## REACTION OF 4-CHLOR-2-IODO-ANILINE WITH BENZOYL CHLORIDE.

Three grams of the 4-chlor-2-iodo-aniline were dissolved in a few c.c. of benzene and about 5 c.c. of benzoyl chloride added. The mixture was warmed on a water bath under a reflux condenser for about twenty minutes. At the end of this time a solid product had formed in the flask. The solid was filtered out and dissolved in hot gasoline, from which it crystallized upon cooling. It was recrystallized from hot alcohol. The melting point was found to be 145°.

The reaction is as follows:




Analysis for iodine and chlorine:

| | | |
|---|---|---|
| Weight watch glass and sample - | 5.0880 g. | 5.0880 g. |
| Weight watch glass alone - - - | 5.0380 | 5.0380 |
| Weight sample used - - - - - - | 0.0500 g. | 0.0500 g. |

Titration:

| | | |
|---|---|---|
| $AgNO_3$ - - Lower reading - - - - | 17.90 | 33.15 |
| Upper reading - - - - | 2.85 | 17.90 |
| Volume $AgNO_3$ solution used - - | 15.05 c.c. | 15.25 c.c. |

| | | |
|---|---|---|
| $NH_4NCS$ - Lower reading - - - - - - | 20.35 | 25.55 |
| Upper reading - - - - - - | 16.55 | 21.40 |
| Volume $NH_4NCS$ solution used - - - - | 3.80 | 4.15 c.c. |

1 c.c. $NH_4NCS$ sol. equals 1 c.c. $AgNO_3$ sol.

| | | |
|---|---|---|
| $AgNO_3$ sol. used to ppt. halogens - | 11.25 | 11.10 c.c. |
| " " " " " iodine - - | 5.62 | 5.55 " |
| " " " " " chlorine - | 5.63 | 5.55 " |

1 c.c. N/40 $AgNO_3$ sol. equals 0.003173 g. iodine.

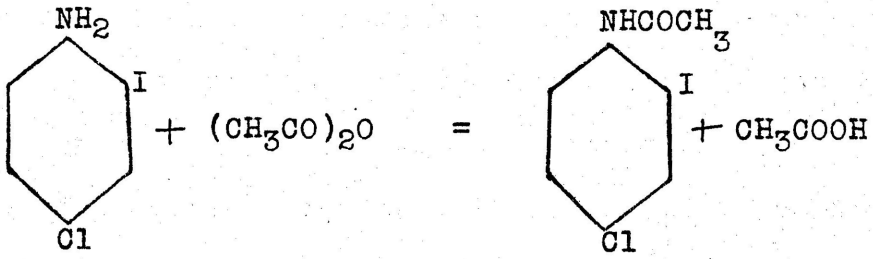
" " " " " " 0.0008865 g. chlorine.

| | | |
|---|---|---|
| Weight of iodine found - - | -0.017848 g. | 0.01761 g. |
| " " chlorine " - - | 0.00499 g. | 0.00492 g. |
| Percent iodine found - - - | 35.70 % | 35.22 % |
| calculated - - - - - | 35.52 % | |
| Percent chlorine found - - - | 9.98 % | 9.84 % |
| calculated -- - - - - | 9.93 %. | |

## REACTION OF 4-CHLOR-2-IODO-ANILINE WITH ACETIC ANHYDRIDE.

Three grams of 2-iodo-4-chlor-aniline were heated with acetic anhydride for about fifteen minutes on a water bath under a reflux condenser. A white crystalline substance was produced. The product was recrystallized from alcohol several times and the melting point found to be 150°.

The reaction is as follows:



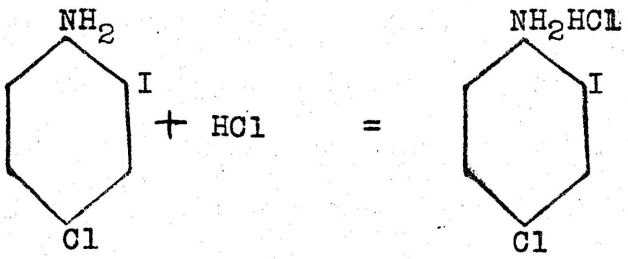

| Analysis for nitrogen: | I | II |
|---|---|---|
| Weight watch glass and sample - | 8.7669 | 5.3380 g. |
| Weight watch glass alone - - - | 8.4651 | 5.0380 |
| Weight sample used - - - - - - | 0.3018 | 0.3000 g. |
| Titration: | | |
| HCl - - - - - - - - - - - - - - - - | 10 c.c. | 10 c.c. |
| NaOH - Lower reading - - - - - | -31.12 | 29.10 |
| Upper reading - - - - - | 24.30 | 21.80 |
| NaOH solution used - - - - - - - | 6.82 c.c. | 7.30 c.c. |
| NaOH factor - - - - - - - - - - | 1.13 | 1.05 |
| HCl used up by $NH_3$ - - - - - - - | 2.29 c.c. | 2.33 c.c. |
| 1 c.c. HCl equals 0.00626 g. $N_2$. | | |
| Weight of $N_2$ found - - - - - - | 0.01434 g. | 0.01458g. |
| Percent $N_2$ found - - - - - - - | 4.75 % | 4.86 % |
| Calculated for $C_8H_7ONICl$ - - - - - - - - | 4.74 %. | |

## REACTION OF 4-CHLOR-2-IODO-ANILINE WITH HYDROGEN CHLORIDE.

Two grams of 4-chlor-2-iodo-aniline were dissolved in benzene and dry HCl gas passed into the solution. A white precipitate formed.

When precipitation was complete, the product was separated from the benzene by filtration. It was dried upon a porous plate and an attempt to determine the melting point showed that it seemed to decompose with the liberation of iodine at about 203°.

The reaction for the formation of the hydrochloride is as follows:




The substance was analyzed for the hydrochloride by dissolving it in alcohol and titrating it with standard NaOH solution.

| Analysis for HCl: | I | II |
|---|---|---|
| Weight watch glass and sample - | 9.7670 | 9.7670 g. |
| Weight watch glass alone - - - | 9.2670 | 9.3290 |
| Weight sample - - - - - - - - - - | 0.5000 | 0.4380 g. |
| Burette readings: - Lower - - - | 48.85 c.c. | 45.45 c.c. |
| Upper - - - | 45.45 | 42.45 |
| NaOH solution used - - - - - - | 3.40 | 3.00 |

1 c.c. NaOH solution equals 0.0184 g. HCl.

Weight of HCl found - - - - - - - 0.0552 g. 0.06256 g.

Percent HCl found - - - - - - - - 12.51 % 12.60 %

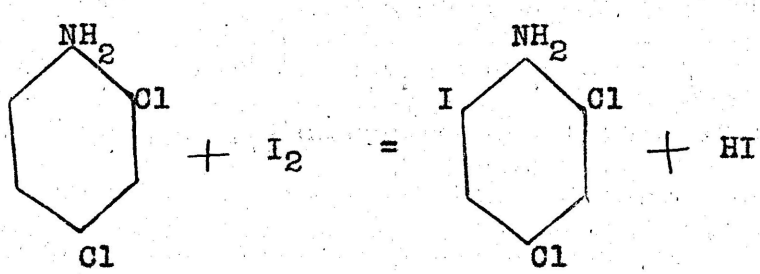
Theoretical percent HCl - - - - - - - - - 12.58 %.

## REACTION OF IODINE WITH 2-4-DICHLORANILINE.

Ten grams of 2-4-dichloraniline, sixteen grams of iodine, ten grams of powdered calcium carbonate, and forty c.c. each of water and ether were mixed in a 250 c.c. wide-mouth flask and heated on a water bath under a reflux condenser for about three hours. A black waxy resinous product was formed which, when treated with benzoyl chloride gave a white crystalline product that melted at 115°. Some of the original dichloraniline was treated with benzoyl chloride and the product obtained had the same melting point. The conclusion was that no iodine had entered the ring to form 2-4-dichlor-6-iodo-aniline as was expected. However, the black waxy resin characteristic of this method was formed.

A second quantity of the dichloraniline was treated as described above but heated for about ten hours. The contents of the flask were then steam distilled. A white crystalline product that melted at 85° was obtained. The melting point of 2-4-dichloraniline is 63°. This product was found to be 2-4-dichlor-6-iodo-aniline. Such a small quantity was obtained that only one reaction was tried, that with dry hydrogen chloride gas.

The following reaction had taken place:




$$CaCO_3 + 2HI = CaI_2 + H_2O + CO_2$$

Analysis for nitrogen:

| | |
|---|---|
| Weight watch glass and sample | 13.2756 g. |
| Weight watch glass alone | 12.9756 |
| Weight sample used | 0.3000 g. |

Titration:

| | |
|---|---|
| HCl | 10 c.c. |
| NaOH - Lower reading | 36.50 |
| Upper reading | 29.15 |
| NaOH solution used | 7.35 c.c. |
| NaOH factor | 1.05 |
| HCl used up by $NH_3$ | 2.28 c.c. |
| 1c.c. HCl equals | 0.00626 g. $N_2$. |
| Weight of $N_2$ found | 0.0147 g. |
| Percent $N_2$ found | 4.76 %. |
| Calculated for $C_6H_4N\ I\ Cl_2$ | 4.83 %. |

Analysis for iodine and chlorine:

| | |
|---|---|
| Weight watch glass and sample | 5.0880 g. |
| Weight watch glass alone | 5.0380 |
| Weight sample used | 0.0500 g. |

Titration:

$AgNO_3$ - - - Lower reading - - - - 27.60
Upper reading - - - - 1.50
$AgNO_3$ solution used - - - - - - - 26.10 c.c.

$NH_4NCS$ - - - Lower reading - - - - 10.25
Upper reading - - - - 4.95
$NH_4NCS$ solution used - - - - - - - 5.30 c.c.

1 c.c. $NH_4NCS$ solution equals 1 c.c. $AgNO_3$ sol.

$AgNO_3$ sol. used to ppt. halogens - 20.80 c.c.

$AgNO_3$ sol. used to ppt. iodine - - 6.93 c.c.

$AgNO_3$ sol. used to ppt. chlorine - 13.86 c.c.

1 c.c. N/40 $AgNO_3$ sol. equals - 0.003173 g. $I_2$.

" " " " " " - 0.0008865 g. $Cl_2$.

Weight of iodine found - - - - - 0.02199 g.

" " chlorine found - - - - 0.012287 g.

Percent iodine found - - - - - - 43.98 %.

" " calculated - - - - 44.09 %.

Percent chlorine found - - - - - 24.57 %.

" " calculated - - - - 24.65 %.

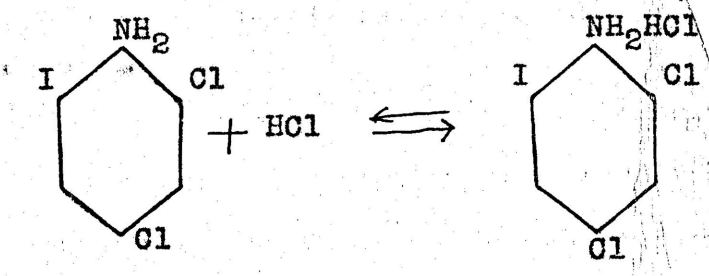
## REACTION OF 2-4-DICHLOR-6-IODO-ANILINE WITH HYDROGEN CHLORIDE.

The 2-4-dichlor-6-iodo-aniline obtained in the preceding preparation was dissolved in benzene and dry hydrogen chloride gas passed through the solution. A precipitate with a pinkish tinge was formed. The precipitate was removed by filtration and dried upon a porous plate.

This hydrochloride is very unstable as it was thoroughly saturated with the gas when it was put upon the porous plate and after about an hour when it appeared to be dry some of it was weighed up and titrated with NaOH solution to determine the percent HCl. Two titrations gave 7.98% and 8.27% respectively. after standing over night, analyses of the same product gave only about 5 % HCl while the theoretical percentage is 11.25 %.

The melting point of the substance was taken some time before the first titration was made and it was found to be 180°. This is probably not the true melting point of the hydrochloride, but the melting point of the hydrochloride mixed with a little of the 2-4-dichlor-6-iodo-aniline.

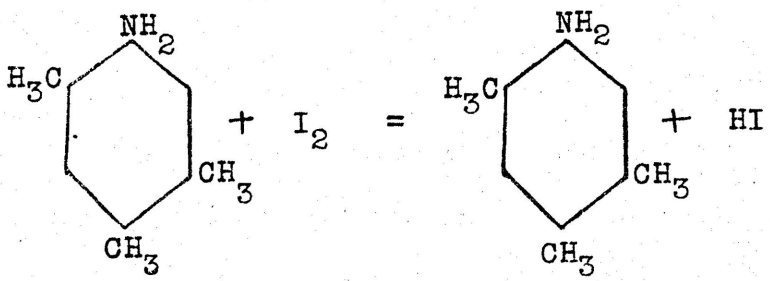
The reaction is as follows:



## REACTION OF IODINE WITH PSEUDO-CUMIDINE.

Ten grams of ps-cumidine, 18 grams of iodine, 10 grams of powdered calcium carbonate, and 50 c.c. each of water and ether were mixed in a 250 c.c. wide-mouth flask and heated on a water bath under a reflux condenser for about three hours. The mixture was then transferred to the steam distillation apparatus and subjected to steam distillation. A quantity of tarry material was left behind in the distilling flask. The material which came over with the water was separated by filtration after cooling and it was found to be a mixture of uncombined ps-cumidine and mono-iodo-ps-cumidine. These two substances were separated by fractional crystallization from gasoline and a small quantity of the mono-iodo-ps-cumidine was obtained. Its melting point is 93°.

The reaction is as follows:




$$CaCO_3 + 2HI = CaI_2 + H_2O + CO_2.$$

| Analysis for nitrogen: | I | II |
|---|---|---|
| Weight watch glass and sample | 7.7464 g. | 7.4368 g. |
| Weight watch glass alone | 7.4368 | 7.0215 |
| Weight sample | 0.3096 g. | 0.4153 g. |
| **Titration:** | | |
| HCl | 25 c.c. | 25 c.c. |
| NaOH - Lower reading | 15.71 | 27.47 |
| Upper reading | 1.45 | 15.71 |
| NaOH solution used | 14.26 | 11.76 |
| NaOH factor | 1.19 | |
| HCl used up by $NH_3$ | 8.02 | 11.00 |
| 1 c.c. HCl equals | 0.0021 g. $N_2$. | |
| Weight of $N_2$ found | 0.0168 g. | 0.0231 g. |
| Percent $N_2$ found | 5.44 % | 5.56 % |
| Calculated for $C_9H_{12}NI$ | 5.36 %. | |

Mono-iodo-pseudo-cumidine has previously been prepared by Kerschbaum* by treating pseudo-cumidine with iodine monochloride. He obtained only a small yield of mono-iodo-pseudo-cumidine and a large amount of resinous material. When he used two moles of ICl the product was practically all resinous material.

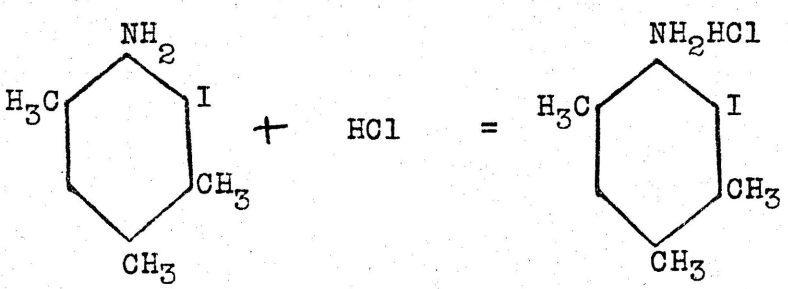
The writer has been able to prepare only a small amount of mono-iodo-pseudo-cumidine by the method under investigation in this work and at the same time a large amount of a tarry resin has been obtained.

* Berichte XXVIII, 2804.

PREPARATION OF MONO-IODO-PSEUDOCUMIDINE HYDROCHLORIDE.

About one and one-half grams of mono-iodo-pseudocumidine were dissolved in benzene and dry hydrogen chloride gas passed through the solution. The hydrochloride of mono-iodo-pseudocumidine formed as a precipitate.

The reaction is as follows:




When precipitation was complete the precipitate was filtered out, dried on a porous plate and the melting point found to be 155°.

The substance was analyzed for HCl by dissolving it in alcohol and titrating with standard NaOH solution.

Analysis for HCl:

| | |
|---|---|
| Weight watch glass and sample - - | 5.6358 |
| Weight watch glass alone - - - - | 5.3885 |
| Weight sample used - - - - - - - | 0.2473 |
| Burette readings: Lower - - - - - | 46.36 |
| Upper - - - - - | .64 |
| NaOH solution used - - - - - - - | 45.72 |

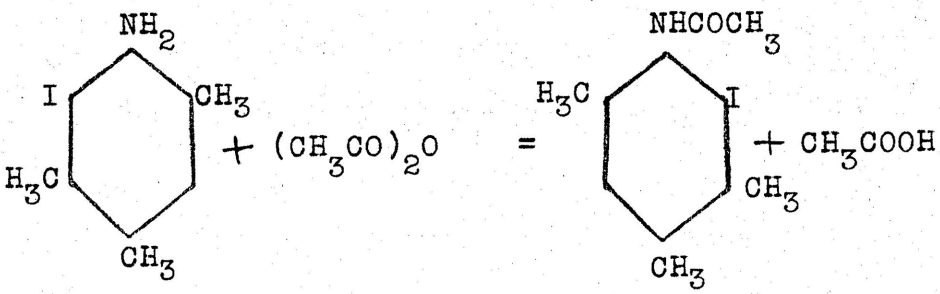
1 c.c. NaOH sol. equals 0.00065 g. HCl.

| | |
|---|---|
| Weight HCl found - - - - - - - - - | 0.02972 g. |
| Percent HCl found - - - - - - - - | 12.02 % |
| Theoretical percent HCl - - - - - | 12.25 %. |

## REACTION OF MONO-IODO-PSEUDO-CUMIDINE WITH ACETIC ANHYDRIDE.

A small quantity of mono-iodo-pseudo-cumidine was treated with acetic anhydride and the acetyl derivative was obtained. This was purified by recrystallizing it from alcohol. The melting point was found to be 192-193°. Not enough of the substance was obtained for further purification and analysis.

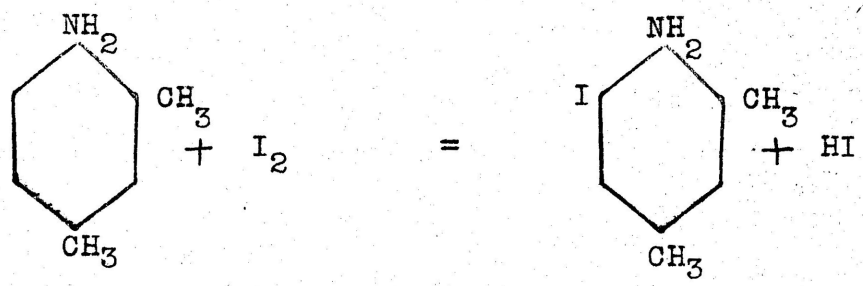
The reaction is as follows:



## REACTION OF IODINE WITH as-m-XYLIDINE.

Ten grams of as-m-xylidine, twenty grams of iodine, ten grams of powdered calcium carbonate, and fifty c.c. each of water and ether were mixed in a 250 c.c. wide-mouth flask and heated on a water bath under a reflux condenser for about two hours. At the end of this time the mixture was transferred to a one-liter flask arranged for steam distillation, and steam passed into it. The distillate was passed through two condensers in series in order to completely condense it. A small amount of product came over and a large amount of tarry material remained behind in the flask. The distillate was allowed to stand until the product separated out, leaving the water clear, and then it was filtered. The product was dissolved in alcohol, heated with animal charcoal to remove some of the color, filtered and poured into ice-cold water in order to precipitate the material.
After filtration the substance was dried on a porous plate. Its melting point was found to be 65°.

The reaction is as follows:



$$CaCO_3 + 2HI \rightarrow CaI_2 + H_2O + CO_2.$$

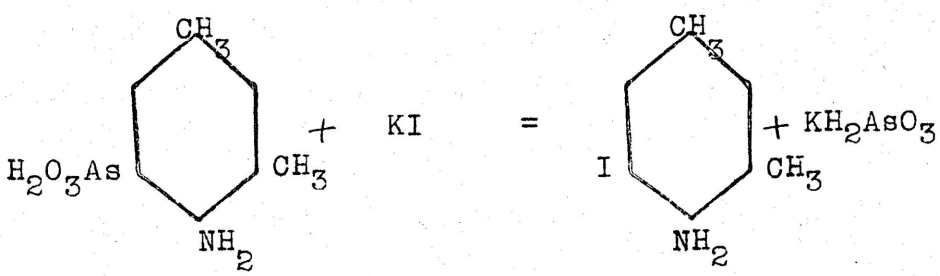
| Analysis for nitrogen: | I | II |
|---|---|---|
| Weight watch glass and sample | 9.0670 | 9.0670 |
| Weight watch glass alone | 8.7670 | 8.7670 |
| Weight sample used | 0.3000 | 0.3000 |
| **Titration:** | | |
| HCl | 10 c.c. | 10 c.c. |
| NaOH - Burette readings: Lower- | 16.85 | 14.30 |
| Upper- | 9.85 | 7.35 |
| NaOH solution used | 7.00 | 6.95 |
| NaOH factor | 1.05 | |
| HCl used up by $NH_3$ | 2.65 c.c. | 2.70 c.c. |
| 1 c.c. HCl equals 0.00626 g. $N_2$. | | |
| Weight of $N_2$ found | 0.01659 g. | 0.0169 g. |
| Percent $N_2$ found | 5.52 % | 5.63 % |
| Calculated for $C_8H_{10}NI$ | 5.67 %. | |

This compound has previously been identified and described by Kerschbaum* who prepared it by treating as-m-xylidine with iodine monochloride. It was later prepared by Benda from 1,3-dimethyl 4-

* Berichte XXVIII, 2799.

amino 5-arsenilic acid.* 2.5 grams of the acid were dissolved in 20 c.c. of water and 20 c.c. of normal NaOH solution and heated on a water bath with 5 grams of potassium iodide and 25 c.c. of twice normal sulphuric acid. After one-half hour it was made alkaline and extracted with ether. Upon evaporation of the ether extract an oil was left behind which soon crystallized to fine needles. He showed this to be identical with the substance previously described by Kerschbaum.

The equation for Benda's reaction is as follows:




* Berichte XLII, 3622.

## SOME GENERAL OBSERVATIONS.

It was found that better results were obtained if the amount of calcium carbonate used was considerably in excess of that theoretically required to combine with the HI liberated in the reaction. For good results the calcium carbonate should be at least equal in weight to the aniline used.

It seems to make no difference whether the iodine is added all at once or a little at a time with heating between additions.

Steam distillation is the most satisfactory method of separating the desired product from the resinous material formed at the same time. It is best to pour the contents directly from the flask in which the reaction is carried out into the steam distilling flask instead of first trying to filter out the calcium carbonate.

If the para position to the $NH_2$ group is free, the iodine will enter the ring in this position much more readily than it will enter the ortho position when the para position is occupied.

More than one $CH_3$ group in the ring seems to have the effect of causing a resinous tar to be

formed instead of the iodine substituted product. This was shown by the action of as-m-xylidine and ps-cumidine, in which cases very little of the desired products were obtained but instead large quantities of black tarry material were produced.

The best method found for removing the color from the product after separating it by steam distillation is to dissolve it in alcohol and boil it with animal charcoal, then filter and precipitate the product by the addition of ice and ice-water.

It was found that the hydrochlorides of the iodine substituted products obtained were not soluble enough in water for successful titration with NaOH solution, but they could be dissolved in alcohol and the alcoholic solution diluted with water and titrated.

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Lawrence, Kansas.